

**Standard Operating Procedure for the Determination of
Gasoline Range Organics (GRO)
in Water and Soil by Purge and Trap
Gas Chromatography/Mass Spectrometry**

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1.0 Scope, Application, and References

1.1 This procedure describes the determination of Gasoline Range Organics (GRO) in water and soil matrices. The determination of GRO in water is based upon EPA Method 524.2. The extraction and determination of GRO in soil is based upon Method SW846 8260B (Revision 2, December 1996). Results can be determined as GRO by carbon range or GRO by individual components. Internal standards, surrogates, and target compounds that can be determined by this procedure are listed below alphabetically along with the Chemistry Division's LIMS analyte number in water, if available. In parenthesis with the target compounds is the number of carbons in that compound.

<u>Internal Standard</u>	<u>Analyte Number</u>
Fluorobenzene	

<u>Surrogates</u>	<u>Analyte Number</u>
4-Bromofluorobenzene	
1,2-Dichlorobenzene-d ₄	

<u>Target Compounds</u>	<u>Analyte Number</u>
1. Benzene (C6)	40500
2. Ethyl benzene (C8)	40880
3. n - Heptane (C7)	
4. Iso - octane (C8)	
5. 2-Methylpentane (C6)	
6. 3-Methylpentane (C6)	
7. MTBE (C5)	40970
8. Naphthalene (C10)	41130
9. Toluene (C7)	40830
10. 1,2,4 - trimethylbenzene (C9)	41105
11. 1,3,5 - trimethylbenzene (C9)	41140
12. 2,2,4 - trimethylpentane (C8)	
13. m - xylene (C8)	40855
14. o - xylene (C8)	40845
15. p - xylene (C8)	40865

1.2 The reporting level for individual components in water is 1.0 ug/L. The reporting level for GRO by carbon range is dependent on the sample. The reporting ranges for soil samples is dependent on sample weight and methanol volume.

2.0 Summary of Method

2.1 Concentrations of GRO's in water and soil are determined by purge and trap GC/MS. Water samples do not require an extraction, but may need to be diluted depending upon the sample. Soil samples are extracted and then aliquots diluted.

2.2 A qualitative GRO analysis is done when the identity of the contaminant is in doubt. Different gasolines may contain the same components but in different ratios, thus allowing tentative identification. In a situation where the source of contamination is suspected or known, a portion of the unadulterated material can be used as a standard.

2.3 A quantitative GRO analysis can be done two different ways. This method primarily covers GRO by individual components.

2.3.1 GRO by carbon range: This method is useful when the contaminant is known and a source is available for use as a standard. In this procedure, standards of known identity and concentrations are analyzed. The sum of the area of all peaks in the in range of MTBE (C5) to naphthalene (C10) is determined. The sum of the area of all peaks in the sample in the same range is determined and the GRO result is calculated versus the standards.

2.3.2 GRO by individual components: This method is useful when the source of contamination is not known and will yield concentrations of some individual components typically found in gasolines. Most commercially available standards contain 9 or 10 components. Gasoline may contain hundreds of components so not all are quantitated.

This method primarily covers GRO by individual components.

3.0 Definitions

3.1 Reagent water - Laboratory purified water that is used to prepare all standard, quality control, and blank solutions.

3.2 Laboratory reagent blank(LRB) - An aliquot of reagent water that is taken and analyzed in the same manner as all standards and samples. The lab blank is used to determine if analytes or other interferences are present in the laboratory environment, reagents, or apparatus.

3.3 Trip blank - Reagent water that is placed in a sample container in the laboratory and included in the shipment to the sample site so it is exposed to the same conditions that samples are. The purpose of the trip blank is to determine if analytes or other interferences are present in the field environment.

3.4 Soil blank - A portion of soil believed to be free of internal standards, surrogates, and target compounds that is extracted and analyzed in the same manner as a soil sample. The soil blank is used primarily to monitor the extraction efficiency of a “clean” sample.

3.5 Laboratory fortified soil blank - A soil blank to which known quantities of analytes are added in the laboratory that is extracted and analyzed in the same manner as a soil sample. The source of analytes must be different than that used to prepare the standards. The purpose of the lab fortified soil blank is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

3.6 Internal standard(IS) - An analyte added to all sample and standard solutions in a known amount and is used to measure the relative response of method analytes and surrogates that are components of the sample or standard solutions.

3.7 Surrogate analyte(Su) - An analyte added to all sample and standard solutions in known amounts and is measured using the same procedures that are used to measure other analytes. The purpose of a surrogate is to monitor method performance with each sample.

3.8 Target compound - An analyte whose concentration can be determined by this procedure.

4.0 Interferences

4.1 Raw analytical data (ion chromatograms) must be evaluated for interferences. Contaminant sources for this procedure are volatile materials present in the laboratory and reagents. The analysis of laboratory blanks provides information about the presence of contaminants. Subtracting blank values from sample results is not permitted.

4.2 Contamination may occur when a sample containing low concentrations of target compounds is analyzed immediately after a sample containing relatively high concentrations of target compounds. Reagent blanks should be analyzed after every sample to minimize this carry over.

4.3 Methylene chloride is a common lab interference. Reagent water should be evaluated early in an analysis to determine if the methylene chloride level is acceptable. One common source of methylene chloride is laboratory clothing such as lab coats that may not have been cleaned for an extended period. The analyst should not wear a lab coat while preparing samples or should wear a recently cleaned coat.

5.0 Safety

5.1 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined, therefore each chemical should be treated as a potential health hazard and exposure to these chemicals should be minimized.

5.2 The following analyte has been tentatively classified as a known or suspected human or mammalian carcinogen: benzene. Pure standard materials and stock solutions of these compounds should be handled in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

5.3 This method does not address all safety issues associated with its use. This laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDS's) should be available to all personnel involved in this analysis.

6.0 Supplies, Equipment, and Instrumentation

Brand names, suppliers, and part numbers are cited for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and materials other than those specified, but equivalent performance must be demonstrated by the laboratory.

6.1 Supplies and Equipment

6.1.1 Ascorbic acid - ACS reagent grade, granular

6.1.2 Liquid nitrogen for cooling of the cryofocuser and the GC oven (optional).

6.1.3 All other supplies and equipment used in this procedure are common to laboratories and will not be detailed here.

6.2 Instrumentation - Instrumentation used in this laboratory as of this revision is detailed as follows:

6.2.1 Gas chromatograph(GC): Hewlett-Packard 5890 Series II equipped with ultra high purity helium gas.

6.2.2 Auto Sampler: Tekmar Dohrmann SOLATek 72 equipped with ultra high purity helium gas.

6.2.3 Concentrator: Tekmar Dohrmann 3100 Purge and Trap sample concentrator equipped with ultra high purity helium gas.

6.2.4 Cryofocuser (Optional): Tekmar Cryofocusing Module.

6.2.5 Detector: Hewlett-Packard 5972 Series Mass Selective Detector(MSD).

6.2.6 Column 1 for use with cryogenic cooling configuration:
J & W DB-5MS, 30 meters x 0.25 mm ID, 0.5 u film thickness
J & W number: 122-5536
Temperature limit: 350 degrees C

6.2.7 Column 2 for use with non-cryogenic cooling configuration:
Agilent DB-624, 25 meters x 0.20 mm ID, 1.12 u film thickness
Agilent number: 128-1324
Temperature limit: 260 degrees C

6.2.8 Data acquisition and analysis: Agilent Chemstation Analysis software.

7.0 **Standard and Quality Control Stock Solutions**

7.1 Internal standard/surrogates stock solution - EPA 524.2 Fortification Solution, Supelco number 4-7932, containing the compounds listed below at 2000 ug/mL in methanol.

Fluorobenzene - Internal Standard (IS)
4-Bromofluorobenzene - Surrogate 1 (S1)
1,2 - Dichlorobenzene-d₄ - Surrogate 2 (S2)

Preparation of IS/Su solution: The SOLATek 72 has 3 IS/Su reservoirs. Use reservoir 3.
Reservoir volume = 22mL
Add 100uL IS/Su stock solution to reservoir 3 and fill reservoir with methanol.

Approximate IS/Su concentrations:

$$2000 \text{ ug/mL} \times 0.10\text{mL}/22\text{mL} = 9.1 \text{ ug/mL}$$

Sample concentration depends on volume added to sample and purge volume.

7.2 Various sources of GRO standards are available for standard and LFB stock solutions. Generally each will contain 9 or 10 target compounds, not necessarily the same or at the same concentration. The table below details 3 different sources, compound names and carbon numbers, and concentration of that compound in the stock. If no concentration is listed, the compound is not present in that standard.

	GRO Mix Supelco No 47576-U	UST Modified GRO Supelco No 4-8167	EPA GRO Supelco No 4-7577-U
<u>Target compound</u>	<u>ug/mL</u>	<u>ug/mL</u>	<u>ug/mL</u>
1. Benzene (C6)	2000	1000	500
2. Ethyl benzene (C8)	2000	1000	500
3. n - Heptane (C7)			500
4. 2-Methylpentane (C6)			1500
5. 3-Methylpentane (C6)	2000		
6. MTBE (C5)		1000	
7. Naphthalene (C10)	2000	1000	
8. Toluene (C7)	2000	1000	1500
9. 1,2,4 - trimethylbenzene (C9)	2000	1000	1000
10. 1,3,5 - trimethylbenzene (C9)		1000	
11. 2,2,4 - trimethylpentane (C8)	2000		1500
12. m - xylene (C8)	2000	1000	1000
13. o - xylene (C8)	2000	1000	1000
14. p - xylene (C8)		1000	

The standards were evaluated in October of 2002 (VOC Notebook 11, pages 158-168 and page 204). The UST modified GRO standards performed the best and will be used as standard and LFB stock solutions. Different ampoules must be used for the standard and LFB stocks.

See Section 12.0 for standard preparation.

See Section 9.1.6 for QC solution preparation.

8.0 Sample collection, Preservation, Shipping, and Storage

8.1 The sample collection procedure depends upon the sample matrix. The following table describes the procedures for various sample types.

<u>Sample Matrix</u>	<u>Container</u>	<u>Preservative</u>	<u>Holding Time</u>
Aqueous with no residual chlorine	40mL amber glass with teflon coated septa, no headspace	80 mg ascorbic acid 2 drops concentrated hydrochloric acid added with sample	14 days
Aqueous with chlorine	40mL amber glass with teflon coated septa no headspace	80 mg ascorbic acid 2 drops concentrated hydrochloric acid added with sample	14 days
Solid samples	Widemouth glass with Teflon-lined lid	Cool to 4 degrees C	14 days
Concentrated Waste Samples	Widemouth glass with Teflon-lined lid	Cool to 4 degrees C	14 days

Source of sample collection information:
SW846, Revision 3, December 1996, Chapter 4, Section 4.1.2, page 7
and EPA Method 524.2.

8.2 Vial preparation

8.2.1 The 40mL amber glass vials are washed with soap and water and rinsed with distilled water. Vials are allowed to dry then are heated in a 100 degree C oven for a minimum of 1 hour.

8.2.2 Remove vials from oven and allow to cool. Inspect each vial for cracks and soap residue. Add about 80 mg ascorbic acid to each vial.

8.2.3 When filling vials, add sample or standard until about half full, then add 2 drops concentrated hydrochloric acid. Fill the vial to overflowing. Cap the vial with open faced caps and teflon-lined septa with the teflon side of the septum in

contact with the sample.

9.0 Quality Control (QC)

9.1 Quality control requirements are the initial demonstration of capability, followed by analysis of lab blanks(LRB), trip blanks, lab fortified blanks (LFB), and other quality control samples with each analysis. The analyst must maintain records to document the quality of the data generated.

9.1.1 Initial demonstration of capability - The data analysis section of this method is similar to EPA Method 524.2. This laboratory has demonstrated proficiency with EPA Method 524.2 so an additional demonstration of capability has not been completed as of this revision.

9.1.2 The procedure for the initial demonstration of capability is as follows:

9.1.2.1 Analyze ten LFB replicates of the UST Modified GRO LFB stock at 2.5 ug/L. See Section 9.1.6 for LFB preparation.
See Section 13 for data analysis procedure.

9.1.2.2 Determine the measured concentration of each target compound in each replicate, the mean concentration of each in all replicates, the mean accuracy (as percentage of mean) for each, and the precision (as relative standard deviation) of the measurements for each target compound.

9.1.2.3 A minimum detection limit(MDL) for each target compound in this method has not been determined. Generally, each target compound will be detectable at either 0.5 ug/L or 1.0 ug/L. Standards must be analyzed to determine which can be used as the reporting level. For each target compound, the mean accuracy should be between 80 and 120%. The precision of the recovery (relative standard deviation) should be less than 20 percent.

9.1.3 An LRB is analyzed during each analysis to determine the interferences present in the reagent water used for standard and LFB preparation. Concentrations of targets present are determined and documented with other QC data. Subtraction of blank levels from samples is not permitted. If soil samples are to be analyzed, a soil LRB is not generally done as soils can differ markedly depending upon their source so the analysis of a soil LRB is not likely to yield

useful information.

9.1.3.1 The LRB must be evaluated for 4-Bromofluorobenzene (BFB) performance and must meet performance criteria. BFB is Surrogate 1. Performance criteria are as follows:

<u>Target Mass</u>	<u>Relative to Mass</u>	<u>Lower Limit %</u>	<u>Upper Limit %</u>
50	95	15	40
75	95	30	60
95	95	100	100
96	95	5	9
173	174	0.00	2
174	95	50	100
175	174	5	9
176	174	95	101
177	176	5	9

The BFB evaluation reports are saved for documentation.

9.1.3.2 A chromatogram of an LRB in water is found in Section 17.

9.1.4 A trip blank for each sample set is analyzed along with the samples. Concentrations of any target compounds in the trip blank are determined. The purpose of the trip blank is to determine if analytes or other interferences are present in the field environment.

9.1.5 An LFB in reagent water is analyzed at the beginning and end of each analysis set. An LFB in reagent water must also be prepared and analyzed if analyzing soils to demonstrate instrument performance.

9.1.6 LFB in water preparation

LFB Stock = UST Modified Gasoline Range Organics

Supelco Stock Number = 4-8167

Target compounds at 1000 ug/mL in methanol, See Section 7.2

This stock solution must be different than that used to prepare the standards.

Prepare an intermediate stock solution at 200 ug/mL:

Dilute stock 200uL/1000uL methanol in a GC autosampler vial.

$1000 \text{ ug/mL} \times 200\text{uL}/1000\text{uL} = 200 \text{ ug/mL}$ each target compound

Then, using a 10uL syringe, transfer 2.5 uL intermediate into a 200 mL flask filled to the mark with water. Concentration is

$200 \text{ ug/mL} \times 0.0025\text{mL}/0.20\text{L} = 2.50 \text{ ug/L}$ each target compound

Performance criteria: The measured concentrations of the target compounds in the LFB must be plus or minus 30% of 2.50 ug/L. If acceptable accuracy cannot be achieved, the problem must be solved before additional samples can be reliably analyzed.

9.1.7 LFB in soil: LFB's in soil are not generally prepared due to the significant concentrations of stocks needed to prepare them as they are diluted. Instead of soil LFB's, previously analyzed QC samples are analyzed and results determined to establish method performance. One example of this is as follows:

Check sample: 02-Q420, from RTC for gasoline in soil determination.

Weigh and record about 10 grams sample into scintillation vial. Add 5 mL methanol. Shake the sample for 2 minutes and allow to settle for at least 30 minutes. Using appropriate syringes/pipettors, dilute sample 0.5 uL, 2.0 uL, 20.0 uL, 100 uL, and 250 uL/200mL water and analyze the dilutions. The range of dilutions will help to ensure that the target compounds are within the calibration range. Transfer the sample to labeled 40mL amber vials with teflon-lined septa for analysis. The vials must have about 80 mg ascorbic acid added prior to the sample and 2 drops of concentrated HCl are added with the aqueous sample. Analyze and determine the concentrations in ug/g. For 02-Q420, assigned values range from about 0.7 to 16.6 ug/g.

10.0 Sample Preparation for Water Samples

10.1 Water samples are analyzed as received unless there is an odor to the sample or there is particulate matter in the sample. If there is an odor to the sample, it should be diluted until there is no odor and then analyzed. If particulate matter is present in the sample, it should be diluted to minimize the risk of plugging the autosampler. Samples should be analyzed over a range of dilutions to help ensure that target compound detections, if any, are within the calibration range.

11.0 Sample Preparation for Soil Samples

11.1 Soil sample preparation can vary depending upon the expected level of target compounds in the sample. The preparation details that follow are intended to be an example.

11.1.1 Mix the sample as much as possible to make it homogeneous.

11.1.2 Weigh and record about 10 g sample into a scintillation vial or a 40 mL amber vial.

11.1.3 Add 10mL methanol to the sample.

11.1.4 Shake the sample for 2 minutes.

11.1.5 Allow the sample to settle for at least 30 minutes.

11.1.6 Dilute the sample with various aliquots to ensure that any target compounds detected will fall within the calibration range. For example, with appropriate syringes and/or pipettors, dilute the sample 0.5uL, 2.0 uL, 20.0 uL, 100uL, and 250uL/200mL water. Transfer the sample to labelled, 40mL amber vials that contain about 80 mg ascorbic acid and add 2 drops of concentrated hydrochloric acid. If any diluted sample has an odor, it must be further diluted before analysis. Analyze the sample and determine target concentrations, if any, in ug/g.

11.1.7 If sample is known to be high in target compounds, less sample can be weighed and/or more methanol can be used to dilute the sample.

11.1.8 If the sample is known to be low in target compounds, more sample can be weighed and/or less methanol can be used to dilute the sample.

12.0 Standard Preparation

Standard Stock Solution: LFB Stock = UST Modified Gasoline Range Organics
Supelco Stock Number = 4-8167
Target compounds at 1000 ug/mL in methanol
See Section 7.2 for target compounds present

Note: This stock solution must be different than that used to prepare the LFB in water, See Section 9.1.6.

12.1 Prepare an intermediate stock solution at 200 ug/mL:

Dilute stock 200uL/1000uL methanol in a GC autosampler vial and store for future use.

Concentration = $1000 \text{ ug/mL} \times 200\text{uL}/1000\text{uL} = 200 \text{ ug/mL}$ each target cpd.

- 12.2 From the stock intermediate, prepare a calibration curve using the dilutions below.

<u>Standard</u>	<u>Dilution</u> <u>in water</u>	<u>Calculation</u>	<u>Final</u> <u>Concentration</u>
GRO Std 1	0.5uL/200mL	$200 \text{ ug/mL} \times 0.0005\text{mL}/0.20\text{L}$	0.50 ug/L each
GRO Std 2	1.0uL/200mL	$200 \text{ ug/mL} \times 0.0010\text{mL}/0.20\text{L}$	1.00 ug/L each
GRO Std 3	2.5uL/200mL	$200 \text{ ug/mL} \times 0.0025\text{mL}/0.20\text{L}$	2.50 ug/L each
GRO Std 4	5.0uL/200mL	$200 \text{ ug/mL} \times 0.0050\text{mL}/0.20\text{L}$	5.00 ug/L each
GRO Std 5	10.0uL/200mL	$200 \text{ ug/mL} \times 0.0100\text{mL}/0.20\text{L}$	10.0 ug/L each
GRO Std 6	20.0uL/200mL	$200 \text{ ug/mL} \times 0.0200\text{mL}/0.20\text{L}$	20.0 ug/L each

12.3 Transfer the standard solutions to 40 mL amber vials with open screw-caps and teflon lined septa. The vials must have about 80 mg ascorbic acid in them prior to the addition of the standard and 2 drops of concentrated hydrochloric acid must be added with the standard solutions.

12.4 A chromatogram of a GRO standard can be found in Section 17.

13.0 Data Acquisition and Analysis

13.1 Data acquisition and analysis is a multi-step process that includes tuning of the mass selective detector(MS), preparing a method for the gas chromatograph(GC), preparing an analysis sequence, preparing the autosampler and concentrator, and installing the liquid nitrogen cooling gas, if necessary. As of this revision this laboratory uses an HP 5890 Series II GC, a Tekmar-Dohrmann SOLATek 72 autosampler, a Tekmar-Dohrmann 3100 sample concentrator, an optional Tekmar Cryofocusing module, an HP 5972 mass selective detector(MS), and Agilent Chemstation Data Analysis software. Conditions will vary depending on if cryogenic cooling is used or not. Conditions for both procedures will be detailed. In some cases, the procedures are the same for the cryogenic and the non-cryogenic procedures. Basic familiarity with the Chemstation Data Analysis software will be assumed.

13.2 Tuning the MS - Hardware tuning the MS is the first step in performing any analysis. The MS is tuned to ensure that the mass to charge ratios are correctly assigned.

13.2.1 Create a new method by updating the name of the most recently used method. Use the format GRyymmdd or CFyymmdd. For example, a method that does not use cryo cooling created on April 22, 2003 would be called CF030422. The CF stands for cryo free.

13.2.2 Perform the Max Sensitivity Autotune in the Tune section of Manual Tune.

13.2.3 Evaluate the tune results. Verify that the peak at mass 69 is the base peak and that peaks at 219 and 502 have detectable responses. Compare the current tune to the previous tune to see if any parameters have had major changes. If any are present, retune the MS and if the changes are still present investigate and correct the problem. The EMVolts should be monitored over the time. As the multiplier ages, the EMVolts will increase. When the EMVolts value approaches 2500, the multiplier may be nearing the end of its usefulness.

13.2.4 Save the tune values as atune.u

13.3 GC preparation - Method Parameters

13.3.1 Typical conditions for procedure using cryogenic cooling

Column: DB-5MS(or equivalent), 30 meters x 0.25mm ID,
0.5u film thickness, column head connected to
cryofocusing module.

J & W part number 122-5536

Max temperature = 350 degrees

Carrier gas: Ultra high purity helium supplied by auxiliary

Channel C; PSI = 12.

Detector B(Interface) = 280 degrees C

Oven temperature program:

0 degrees C for 5 minutes

6 degrees C/min to 70 degrees C, hold for 0 min

15 degrees C/min to 145 degrees C, hold for 2.50 min

30 degrees C/min to 265 degrees C, hold for 5.00 min

Total run time: 33.17 minutes

Cryo: On

The transfer line from the Tekmar 3100 is directly connected to the column head at the cryofocusing unit. The conventional injection ports are bypassed.

13.3.2 Typical conditions for procedure without cryogenic cooling

Column: DB-624(or equivalent), 25 meters x 0.2 mm ID,
1.12u film thickness, connected to inlet A
Agilent part number 128-1324
Maximum temperature = 260 degrees
E psi: 45; Supplies carrier to inlet A
Carrier gas: Ultra high purity helium to inlet A, through auxiliary E
Inlet A temperature: 210 degrees C
Inlet A liner: Glass, deactivated, direct, 2mm ID
Agilent number: 5181-8818
C psi: 0
Oven temperature program:
35 degrees C for 2 min
5 degrees C/min to 145 degrees C, hold for 0 min
30 degrees C/min to 230 degrees C, hold for 5 min
Total run time = 31.83 min
Detector B(Interface) = 280 degrees C
Cryo: Off
Mode: Constant Pressure
Pressure program:
9 psi for 0.15 min
7.5 psi/min to 15 psi, hold for 30.88min
Total program time = 31.83 min
Purge: Initial = On, Off at 1.25 min

13.3.3 MS Acquisition parameters

Acquisition mode: Scan
Solvent Delay: 0.00 min
EM Absolute: false
EM offset: 0
Low mass: 40
High mass: 300
Threshold: 150
Sample #: 2
A/D samples: 4

Additional MS acquisition parameters such as retention times, quant ions, and qualifier ions will be listed in Section 17, Table 1.

13.4 Preparation of Chemstation Sequence

13.4.1 After completion of the Chemstation data analysis method, the Chemstation sequence is prepared using the Quick Sequence Generator. Supply the requested information to build the analysis. Save the sequence under the same name as the method. Standards are generally analyzed at the beginning and end of each analysis. An LFB is also analyzed at the beginning and end of each analysis.

13.4.2 After the detector has been tuned (Section 13.2), the GC method has been established (Section 13.3) and the sequence prepared and loaded (Section 13.4), the GC and software are ready for the analysis to begin after completion of the autosampler programming.

13.5 Preparation of the SOLATek 72 and the Tekmar 3100

13.5.1 The SOLATek 72 functions as the autosampler for the purge and trap system and the Tekmar 3100 functions as the purge and trap apparatus. Both are programed in the Tekmar software at the workstation. A method and schedule are necessary to start the analysis. Typical method parameters for the procedures with and without cryo cooling are as follows:

<u>Parameter</u>	<u>With Cryo</u>	<u>Without Cryo</u>
Sample purge volume	25 mL	25 mL
Internal standard volume	5 uL	5 uL
SOLATek 72		
Rinse water temp	90 deg C	90 deg C
Sample cup temp	30 deg C	30 deg C
Sample needle temp	30 deg C	30 deg C
Transfer line temp	125 deg C	125 deg C
Soil valve temp	125 deg C	125 deg C
Sample sweep time	0.50 min	0.50 min
Needle sweep time	1.00 min	1.00 min
Needle rinse volume	15 mL	15 mL
Bake rinse volume	15 mL	15 mL
Bake sweep time	1.00 min	1.00 min
Bake drain time	1.00 min	1.00 min

Number of bake rinses	1	1
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Tekmar 3100

Valve oven temp	175 deg C	125 deg C
Transfer line temp	175 deg C	125 deg C
Sample mount temp	45 deg C	45 deg C
MCS temp	35 deg C	35 deg C
MCS bake temp	310 deg C	310 deg C
Purge ready temp	33 deg C	33 deg C
Purge temp	0 deg C	0 deg C
Turbo cool temp	- 20 deg C	- 20 deg C
GC start	End of desorb	Start of desorb
GC cycle time	0.00 min	0.00 min
Sample heater	Off	Off
Sample temp	40 deg C	40 deg C
Sample preheat time	0.00 min	0.00 min
Purge time	10.00 min	11.00 min
Dry purge time	3.00 min	2.00 min
Desorb preheat temp	245 deg C	250 deg C
Desorb time	5.00 min	4.00 min
Desorb temp	255 deg C	260 deg C
Bake time	15.00 min	15.00 min
Bake temp	265 deg C	265 deg C
Cryofocuser	On	Off
Cryo standby temp	150 deg C	Not applicable
Cryo focus temp	- 150 deg C	Not applicable
Cryo inject time	0.45 min	Not applicable
Cryo inject temp	235 deg C	Not applicable

13.5.2 Prepare a schedule on the SOLATek 72 program to analyze the samples. The analysis can be started as soon as enough samples are in place and can run while the rest of the samples/standards are being prepared.

13.5.3 Verify that sufficient internal standard/surrogates solution is in the reservoir on the SOLATek 72. If not, prepare new spiking solution as indicated in Section 7.1.

13.5.4 Add the samples to the SOLATek 72.

13.5.5 Prime the internal standard/surrogates solution and the rinse water before starting the schedule.

13.5.6 Check waster reservoirs to be sure there is sufficient room for waste volume.

13.5.7 Begin the analysis by pressing the start button in the SOLATek 72 program. The liquid nitrogen should be connected immediately if required.

13.6 Installation and application of the liquid nitrogen for cooling, if necessary.

13.6.1 Liquid nitrogen is supplied in gas-paks, low pressure delivery devices. A union is provided at the top of the gas-pak for connection to the cryo-focusing module at the top of the GC.

13.6.2 Connect the nitrogen supply and open the valve on the gas pak.

13.6.3 The GC oven temperature should be at 200 degrees C when the analysis is started on the SOLATek 72. When the purging of the first sample reaches the Dry Purge stage, the GC oven temperature must be set to 0 degrees on the keypad of the GC. This is the only time this must be done.

13.7 Data processing of standards should be done as soon as possible to determine if any problems are present. A calibration curve should be prepared from the first set of standards and the first LFB injection should be analyzed versus the curves to monitor progress. Samples should be monitored as analysis progresses to determine if any need dilutions and to see if surrogate recoveries are acceptable. A second LFB is analyzed at the end of the analysis. If both LFB's pass using Standard Set 1 only, the second set does not need to be included in the calibrations.

14.0 Method Performance

14.1 The reporting level for individual GRO components in water is 1.0 ug/L. The reporting level for individual GRO components in soil will vary depending upon sample weight and methanol volume.

14.2 A quality control sample of gasoline in soil was analyzed by this procedure in November 2002. The results are listed below. A chromatogram of the sample and a standard chromatogram can be found in Section 17.

Sample: 02-Q420
Standard: UST Modified GRO

<u>Analyte</u>	<u>Reported Result</u>	<u>Assigned Value</u>	<u>Percent Recovery</u>
benzene	2.66 mg/Kg	3.15 mg/Kg	84
ethylbenzene	3.43	3.62	95
toluene	15.6	14.6	107
xylene, total	15.3	16.6	92
m + p-xylene	11.3	12.5	90
o-xylene	4.00	4.49	89
MTBE	1.49	2.87	52
naphthalene	0.65	0.74	88
Gasoline			
Range Organics	39.13	185	21

Note that the sum of the individual components, 39.13 mg/Kg is 21% of the assigned GRO value of 185 mg/Kg. This is because only 7 of the hundreds of components in the gas were quantitated. This procedure should not be used for determining a GRO value. If a GRO result is desired, the carbon range procedure described briefly in Section 2.3.1 is the preferred method.

15.0 Pollution Prevention

15.1 No solvents are used in this method except the small volumes of methanol needed to make standards and for soil samples. The only other chemicals used are the method target compounds and they are present in small amounts that pose minimal threat to the environment.

16.0 Waste Management

16.1 Excess standards and samples may be disposed of by rinsing down a drain with tap water. For soil samples, the methanol from the samples can be evaporated in a hood and the dry soil can be discarded in the trash.

16.2 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions. The laboratory has the responsibility to protect the environment by minimizing and controlling all releases from fume hoods and bench operations.

17.0 Tables and Chromatograms

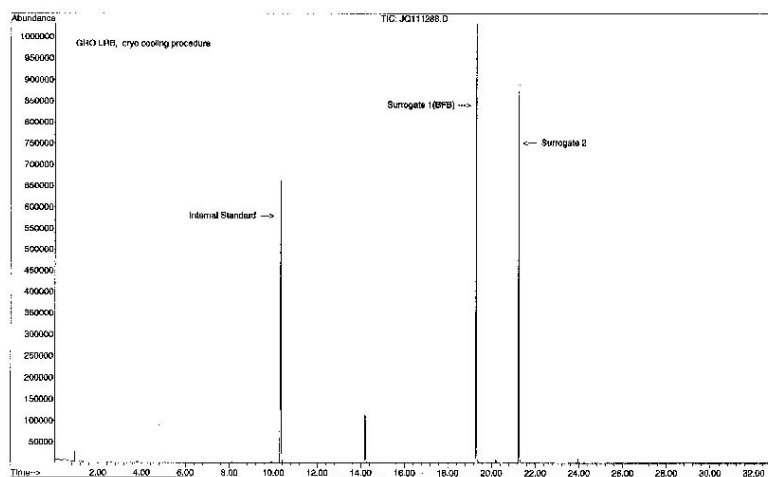
17.1 Table 1: Target compound retention times, quant ions, and qualifier ions

Peak	Compound	R _t (min)	Quant Ion	Qualifier Ions (Percent Q Ion)
1.	Fluorobenzene	10.37	96.0	70.1(20.5), 75.1(6.7)
2.	4-Bromofluorobenzene	19.32	95.0	173.9(84.4), 175.9(81.0)
3.	1,2-Dichlorobenzene-d ₄	21.25	152.0	115.1(63.5), 150.0(155.1)
4.	2-Methylpentane (C6)	5.16	43.1	42.05(54.8), 71.1(32.1) 57.0(12.5)
5.	MTBE (C5)	5.35	73.0	43.1(38.2), 57.0(18.0)
6.	3-Methylpentane (C6)	5.79	57.0	56.0(96.1), 55.0(14.3)
7.	Benzene (C6)	9.56	78.0	77.0(24.4)
8.	n - Heptane (C7)	11.54	43.1	57.0(43.2), 71.1(48.5), 100.1(11.4)
9.	Toluene (C7)	14.20	92.0	91.0(176.7)
10.	Ethylbenzene (C8)	17.65	91.0	106.0(24.9)
11.	m - xylene (C8)	17.91	106.0	91.0(273.5), 105.0(47.5)
12.	p - xylene (C8)	17.95	106.0	91.0(252.9), 105.0(48.6)
13.	o - xylene (C8)	18.50	106.0	91.0(283.2), 105.0(43.3)
14.	1,3,5 - trimethylbenzene (C9)	20.14	105.0	120.1(37.1)
15.	1,2,4 - trimethylbenzene (C9)	20.59	105.0	120.1(38.5)
16.	Naphthalene (C10)	23.72	128.5	None
17.	2,2,4 - trimethylpentane (C8)	NA	NA	NA

NA = Not available

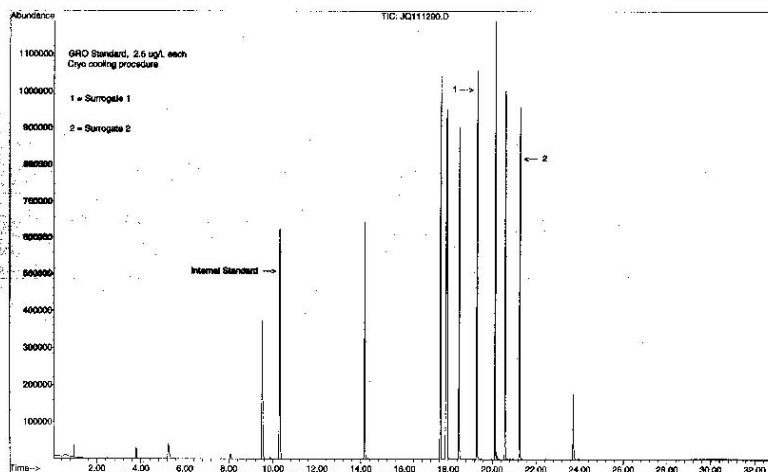
17.2 Chromatogram 1: Cryo procedure, LRB

File : D:\HPCHEM\1\DATA\VC021112\JQ111288.D
Operator :
Acquired : 15 Nov 2002 11:44 am using AcqMethod VC021112
Instrument : HPMSD1
Sample Name: water
Misc Info :
Vial Number: 88



17.3 Chromatogram 2: Cyro procedure, GRO Standard, 2.50 ug/L each

File : D:\HPCHEM\1\DATA\VC021112\JQ111290.D
Operator :
Acquired : 15 Nov 2002 1:20 pm using AcqMethod VC021112
Instrument : HPMSD1
Sample Name: M-GRO Std 2.5 ug/L
Misc Info :
Vial Number: 90



17.4 Chromatogram 3: Cryo procedure, 02-Q420 and GRO Standard

File : D:\HPCHEM\1\DATA\VC021112\JQ111289.D
Operator :
Acquired : 15 Nov 2002 12:32 pm using AcqMethod VC021112
Instrument : HPMSD1
Sample Name: M-GRO Std 1.0ug/L
Misc Info :
Vial Number: 89

